

Alkyne–Alkyne Coupling Reactions with $W(CO)(PhC\equiv CPh)_3$ and $W(NCMe)(PhC\equiv CPh)_3$

Wen-Yann Yeh,* Chi-Lin Ho, Michael Y. Chiang,[†] and I-Ting Chen

Department of Chemistry, National Sun Yat-Sen University, Kaohsiung, Taiwan 80424

Received March 24, 1997[⊗]

Heating $W(CO)(PhC\equiv CPh)_3$ (**1**) and diphenylacetylene in a sealed tube leads to alkyne–alkyne coupling to yield $W(CO)(PhC\equiv CPh)_2(\eta^4-C_4Ph_4)$ (**2**), $W(CO)(PhC\equiv CPh)(\eta^5-C_3Ph_3(C_5Ph_5))$ (**3**), and $W(CO)(PhC\equiv CPh)(\eta^6-C_3Ph_3(C_5Ph_5))$ (**4**) together with the tungstenocene oligomer $[W(C_5Ph_5)_2]_x$ (**5**). Oxidation of **5** by diiodine affords $W(\eta^5-C_5Ph_5)_2(I)_2$ (**6**), which is converted into the oxo complex $W(\eta^5-C_5Ph_5)_2(=O)$ (**7**) by treating with $AgBF_4$ in wet dichloromethane solution. Reaction of $W(NCMe)(PhC\equiv CPh)_3$ (**8**) and 1 equiv of diphenylacetylene produces $W(NCMe)(PhC\equiv CPh)_2(\eta^4-C_4Ph_4)$ (**9**), whereas a similar reaction in the presence of excess diphenylacetylene gives mainly the metallacyclic complex $W(PhC\equiv CPh)(\eta^8-C_8Ph_8)$ (**10**). Compound **10** reacts with carbon monoxide to afford **3** and **4**, while thermolysis of pure **10** results in **5** exclusively. The reaction mechanism has been explored by C-13 labeling experiments. The structures of **7** and **10** have been established by an X-ray diffraction study. The bonding of pentaphenylcyclopentadienyl ligands of **7** is best described as a localized $\eta^3:\eta^2$ fashion. Compound **10** contains a tungstenacyclononapentaene ring with two tungsten–carbon double bonds.

Introduction

Mechanistic steps involving the formation of metallacycles, and their interconversions and subsequent decay, are implicated in a number of important catalytic transformations.¹ It has been shown that reactions of alkynes with transition-metal compounds can lead to di-, tri-, or tetramerization of the alkyne ligands, and in doing so they lose their individuality, forming metallacyclic systems or carbocycles.² Nevertheless, an isolable metal complex, which would confirm the linking of acetylene units, is not obtained in all cases. We previously communicated the reaction of $W(L)(PhC\equiv CPh)_3$ ($L = CO, NCMe$) and diphenylacetylene to yield cyclobutadiene complexes, $W(L)(PhC\equiv CPh)_2(\eta^4-C_4Ph_4)$,³ and a cyclopentadienylpropenylidene complex, $W(CO)(PhC\equiv CPh)(\eta^5-C_3Ph_3(C_5Ph_5))$.⁴ Two questions were raised: whether the butadiene group is derived from the coordinated $PhC\equiv CPh$ ligands or the added diphenylacetylene is involved and how the five-membered cyclopentadiene ring is assembled. Presented in this article are complete characterizations of the reaction products and information concerning the alkyne–alkyne coupling mechanism. A novel metallacyclononapentaene intermediate and a tungstenocene oxo

derivative have also been produced and structurally characterized.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of purified nitrogen with standard Schlenk and syringe techniques.⁵ Solvents were distilled from the appropriate drying agent before use.⁶ $W(CO)(PhC\equiv CPh)_3$ (**1**)⁷ and $W(NCMe)(PhC\equiv CPh)_3$ (**8**)⁸ were prepared by literature methods. $Ph^{13}C\equiv CPh$ was prepared from $Ph_2^{13}C(=O)$ as described in the literature.⁹ Diphenylacetylene, diiodine, and silver tetrafluoroborate ($AgBF_4$) were purchased from Aldrich and used as received. Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Merck, GF 254). ¹H and ¹³C NMR spectra were obtained on a Varian VXR-300 spectrometer at 300 and 75.4 MHz, respectively. IR spectra were taken on a Hitachi-2001 spectrometer. Fast-atom bombardment (FAB) and electron impact (EI) mass spectra were obtained on a VG-5022 mass spectrometer. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at National Chen-Kung University, Tainan, Taiwan. Single-crystal X-ray diffraction studies were conducted on a Rigaku AFC6S diffractometer with graphite-monochromated Mo K α radiation using the ω – 2θ scan technique.

Reaction of 1 and Molten $PhC\equiv CPh$. $W(CO)(PhC\equiv CPh)_3$ (**1**; 500 mg, 0.67 mmol) and diphenylacetylene (340 mg, 1.91 mmol) were mixed, ground, and sealed in a glass tube under vacuum (0.1 mmHg). The tube was placed in a silicon oil bath at 120 °C. During the first 1 min of reaction, vigorous bubbling of CO gas was observed with formation of a dark red solution (Note: diphenylacetylene melts at 60 °C). After 25 min, the

[†] To whom inquiries concerning the X-ray crystallographic work should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts*, May 15, 1997.

(1) (a) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1994. (c) Katz, T. J. *Adv. Organomet. Chem.* **1977**, *16*, 283. (d) Chapell, S. D.; Cole-Hamilton, D. J. *Polyhedron* **1982**, *1*, 739. (e) Chisholm, M. H.; Heppert, J. A. *Adv. Organomet. Chem.* **1986**, *26*, 97. (f) Chien, J. C. W. *Coordination Polymerization*; Academic Press: New York, 1975. (g) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(2) Grotjahn, D. B. In *Comprehensive Organometallic Chemistry II*; Pergamon: Oxford, U.K., 1995; Vol. 12, p 741, and references therein.

(3) Yeh, W.-Y.; Liu, L.-K. *J. Am. Chem. Soc.* **1992**, *114*, 2267.

(4) Yeh, W.-Y.; Peng, S.-M.; Lee, G.-H. *J. Chem. Soc., Chem. Commun.* **1993**, 1056.

(5) Shriver, D. F.; Drezdson, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

(6) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, U.K., 1988.

(7) (a) Tate, D. P.; Augl, J. M. *J. Am. Chem. Soc.* **1963**, *85*, 2174. (b) Tate, D. P.; Augl, J. M.; Ritchey, W. M.; Rose, B. L.; Grasselli, J. G. *J. Am. Chem. Soc.* **1964**, *86*, 3261.

(8) Yeh, W.-Y.; Ting, C.-S.; Chih, C.-F. *J. Organomet. Chem.* **1991**, *427*, 257.

(9) Colvin, E. W.; Hamill, B. J. *J. Chem. Soc., Perkin Trans. I* **1977**, 869.

tube was removed from the bath, cooled to room temperature, and opened in air. The resulting brown-red residue was extracted with dichloromethane (3 × 10 mL) to give a deep red solution and orange-red solids. The extract was concentrated to ca. 5 mL on a rotary evaporator and applied to TLC with hexane/dichloromethane (3:1, v/v) as eluant. The unreacted diphenylacetylene was recovered from the first, colorless band. The material from the second, orange-red band afforded W(CO)(PhC≡CPh)₂(η⁴-C₄Ph₄) (**2**; 249 mg, 0.27 mmol, 40%). The third, red band gave W(CO)(PhC≡CPh)(η⁵-C₃Ph₃(C₅Ph₅)) (**3**; 98 mg, 0.09 mmol, 13%). The material from the fourth, purple band yielded W(CO)(PhC≡CPh)(η⁶-C₃Ph₃(C₅Ph₅)) (**4**; 45 mg, 0.04 mmol, 6%).

The dichloromethane-insoluble solids were washed with methanol, THF, and *n*-hexane and dried under vacuum overnight. This orange-red material was formulated as [W(C₅Ph₅)₂]_x (**5**; 230 mg, 32%), on the basis of spectroscopic characterization and reaction with I₂ to give W(η⁵-C₅Ph₅)₂(I)₂ (**6**).

Characterization of 2. IR (KBr disk): 2030 (ν(CO)) 1595 (ν(C≡C)) cm⁻¹. Mass spectrum (FAB): *m/z* 924 (M⁺, ¹⁸⁴W), 896 (M⁺ - CO), 718 (M⁺ - CO - C₂Ph₂), 540 (M⁺ - CO - 2C₂Ph₂). ¹H NMR (CD₂Cl₂, 25 °C): δ 7.25–6.77 (m, Ph). ¹³C{¹H} NMR (CDCl₃, 25 °C): δ 214.9 (CO), 175.9, 158.9 (C≡C), 140.6–125.1 (m, C₆H₅), 83.8 (C₄Ph₄). Anal. Calcd for C₅₇H₄₀OW: C, 74.03; H, 4.36. Found: C, 74.33; H, 4.60.

Characterization of 3. IR (KBr disk): 2005 (ν(CO)), 1602 (ν(C≡C)) cm⁻¹. Mass spectrum (FAB): *m/z* 1102 (M⁺, ¹⁸⁴W), 1074 (M⁺ - CO), 1025 (M⁺ - Ph), 997 (M⁺ - Ph - CO), 896 ((M⁺ - CO - C₂Ph₂)). ¹H NMR (CDCl₃, 20 °C): δ 7.78–5.15 (m, Ph). ¹³C{¹H} NMR (CDCl₃, 20 °C): δ 300.8 (W=C, ¹J_{W-C} = 140 Hz), 220.0 (CO), 197.4, 190.0 (C≡C), 159.7, 150.3, 111.8, 98.5, 95.1, 81.9, 29.7 (C₈Ph₈), 142.7–120.89 (m, C₆H₅). Anal. Calcd for C₇₁H₅₀OW: C, 77.31; H, 4.57. Found: C, 77.12; H, 4.60.

Characterization of 4. IR (C₆H₁₂, ν(CO)): 1932 cm⁻¹. Mass spectrum (FAB): *m/z* 1102 (M⁺, ¹⁸⁴W), 1074 (M⁺ - CO), 896 (M⁺ - CO - C₂Ph₂). ¹H NMR (CDCl₃, 20 °C): δ 8.30–5.40 (m, Ph). ¹³C{¹H} NMR (CDCl₃, 20 °C): δ 236.4 (s, CO), 206.3 (s, C≡), 204.2 (s, C≡), 172.6, 157.7, 127.0, 126.1, 117.6, 93.6, 68.0, 29.7 (C₈Ph₈), 150.6–124.1 (m, C₆H₅). Anal. Calcd for C₇₁H₅₀OW: C, 77.31; H, 4.57; O, 1.45. Found: C, 77.46; H, 4.79; O, 1.17.

Characterization of 5. Mass spectrum (EI, 350 °C, 70 eV): *m/z* 1074 (¹⁸⁴W(C₅Ph₅)₂). IR (KBr pellet): 3060, 1602, 1505, 1448, 1072, 1026, 800, 780, 736, 702, 556 cm⁻¹. Anal. Calcd for (C₇₀H₅₀W)_x: C, 78.21; H, 4.68. Found: C, 77.84; H, 4.72.

Preparation of 6. An oven-dried, three-necked spherical flask (100 mL) was equipped with a magnetic stirbar, a rubber serum stopper, a reflux condenser, and a nitrogen inlet. When the stopper was briefly removed, a sample of [W(η⁵-C₅Ph₅)₂]_x (**5**; 300 mg, 0.28 mmol based on W) and benzene (40 mL) were introduced against a nitrogen flow. The mixture was brought to reflux under nitrogen, and I₂ (89 mg, 0.35 mmol) in benzene (10 mL) was added dropwise over 10 min via a syringe. The mixture was kept refluxing for 1 h, cooled to ambient temperature, and filtered. The green residue was washed with benzene (2 × 5 mL) and then extracted with dichloromethane (2 × 15 mL) to give a dark green solution. The extract was filtered, concentrated to ca. 5 mL under vacuum, and layered with benzene (15 mL), resulting in dark green crystals of W(η⁵-C₅Ph₅)₂(I)₂ (**6**; 327 mg, 0.25 mmol, 88%). IR (KBr): 3064, 1604, 1506, 1450, 1408, 1264, 1078, 1028, 968, 906, 800, 778, 740, 710, 700 cm⁻¹. ¹H NMR (CDCl₃, 20 °C): δ 7.10–6.79 (m, Ph). Mass spectrum (FAB): *m/z* 1074 (M⁺ - 2 I). Anal. Calcd for C₇₀H₅₀I₂W: C, 63.27; H, 3.79. Found: C, 62.63; H, 3.90.

Preparation of 7. A 50 mL Schlenk flask was charged with W(η⁵-C₅Ph₅)₂(I)₂ (**6**; 90 mg, 0.068 mmol), AgBF₄ (26 mg, 0.13 mmol), dichloromethane (10 mL), and water (100 μL). The mixture was stirred at room temperature for 1 h, affording a deep green solution and pale yellow precipitates of AgI. The

solution was filtered, concentrated to ca. 3 mL under vacuum, layered with benzene (10 mL), and placed in a freezer at -20 °C overnight to give dark green crystals of W(η⁵-C₅Ph₅)₂(=O) (**7**; 42 mg, 0.038 mmol, 56%). IR (KBr): 3064, 1604, 1504, 1448, 1182, 1076, 1028, 802, 778, 740, 700 (C–C, C–H), 906 (ν(W=O)) cm⁻¹. ¹H NMR (CD₂Cl₂, 20 °C): δ 7.70–6.65 (m, Ph). ¹³C{¹H} NMR (CD₂Cl₂, 20 °C): δ 134.2 (C₅Ph₅), 133.1, 130.6, 129.3, 128.8 (Ph). Mass spectrum (FAB): *m/z* 1090 (M⁺, ¹⁸⁴W), 1074 (M⁺ - O). Anal. Calcd for C₇₀H₅₀OW: C, 77.06; H, 4.62. Found: C, 77.42; H, 4.60.

Crystals of **7** found suitable for an X-ray diffraction study were grown from dichloromethane/benzene at -20 °C.

Reaction of 8 and 1 Equiv of PhC≡CPh. A 50 mL Schlenk flask containing W(NCMe)(PhC≡CPh)₃ (**8**; 500 mg, 0.66 mmol) and diphenylacetylene (118 mg, 0.66 mmol) were purged with dry N₂. 1,2-Dichloroethane (20 mL) was added, and the flask was attached to a reflux condenser equipped with a mineral oil bubble. The mixture was heated to reflux (101 °C) for 15 min, cooled to room temperature, and evaporated to dryness under vacuum. The residue was dissolved in dichloromethane and separated by TLC, with hexane/dichloromethane (4:1, v/v) as eluant. Isolation of the material forming the major orange-red band gave W(NCMe)(PhC≡CPh)₂(η⁴-C₄Ph₄) (**9**; 480 mg, 0.51 mmol, 77%). Mp: 175–177 dec. IR (KBr): 1591 (ν(C≡C)) cm⁻¹. Mass spectrum (FAB): *m/z* 937 (M⁺, ¹⁸⁴W), 896 (M⁺ - NCMe), 718 (M⁺ - NCMe - C₂Ph₂), 540 (M⁺ - NCMe - 2C₂Ph₂). ¹H NMR (CD₂Cl₂, 25 °C): δ 7.33–6.78 (m, Ph), 1.90 (s, CH₃CN). ¹³C{¹H} NMR (CD₂Cl₂, 25 °C): δ 186.5, 174.8 (C≡C), 140.8–124.8 (Ph, N≡C), 86.2 (C₄Ph₄), 4.4 (CH₃). Anal. Calcd for C₅₈H₄₃NW: C, 74.28; H, 4.62; N, 1.49. Found: C, 74.49; H, 4.70; N, 1.47.

Reaction of 8 and 1 Equiv of Ph¹³C≡CPh. This reaction was carried out and worked up in a fashion identical with that above. The ¹³C{¹H} NMR spectrum of the product revealed an intense signal at δ 86.2 corresponding to the resonance of cyclobutadiene ring carbons. The intensities of other ¹³C resonance signals were not affected.

Reaction of 8 with Excess PhC≡CPh. A 50 mL Schlenk flask containing W(NCMe)(PhC≡CPh)₃ (**8**; 200 mg, 0.26 mmol) and diphenylacetylene (240 mg, 1.34 mmol) was purged with dry N₂. Toluene (10 mL) was added, and the flask was attached to a reflux condenser equipped with a mineral oil bubble. The mixture was heated to reflux (110 °C) for 8 min and then quickly cooled down by placing the flask in an ice bath. The solution was evaporated to dryness under vacuum. The residue was extracted with dichloromethane (2 × 10 mL) to give a dark red solution and orange-red solids [W(C₅Ph₅)₂]_x (**5**; 20 mg, 7%). The extract was concentrated to ca. 3 mL on a rotary evaporator and subjected to TLC, with hexane/dichloromethane (7:3, v/v) as eluant. The unreacted diphenylacetylene was recovered from the first, colorless band. The material forming the third, orange-red band gave W(NCMe)(PhC≡CPh)₂(η⁴-C₄Ph₄) (**9**; 46 mg, 0.049 mmol, 19%). Isolation of the material from the second, red band afforded W(PhC≡CPh)(η⁸-C₈Ph₈) (**10**; 116 mg, 0.108 mmol, 42%). Mass spectrum (FAB): *m/z* 1074 (M⁺, ¹⁸⁴W), 896 (M⁺ - C₂Ph₂). ¹H NMR (CDCl₃, 20 °C): δ 7.42–6.16 (m, Ph). ¹³C{¹H} NMR (CDCl₃, 20 °C): δ 240.3 (W=C, ¹J_{W-C} = 96 Hz), 196.8, 189.5 (C≡C), 130.0, 126.5, 93.5 (s, C₈Ph₈), 150.0–124.6 (m, Ph). Anal. Calcd for C₇₀W₅₀W: C, 78.21; H, 4.68. Found: C, 77.69; H, 4.80.

Crystals of **10** found suitable for X-ray diffraction study were grown by slow diffusion of benzene into dichloromethane solution at -20 °C for 1 week.

Reaction of 9 and PhC≡CPh. A 50 mL Schlenk flask was attached to a reflux condenser equipped with a mineral oil bubble. W(NCMe)(PhC≡CPh)₂(η⁴-C₄Ph₄) (**9**; 100 mg, 0.1 mmol), diphenylacetylene (127 mg, 0.7 mmol), and toluene (5 mL) were added into the flask. The mixture was heated to reflux under nitrogen for 15 min, cooled to ambient temperature, and evaporated to dryness under vacuum. The residue was dissolved in dichloromethane and separated by TLC, with

dichloromethane/hexane (3:7, v/v) as eluant. W(PhC≡CPh)(η^8 -C₈Ph₈) (**10**) was obtained in 16% yield (17 mg, 0.016 mmol).

Thermolysis of 10. A red solution of W(PhC≡CPh)(η^8 -C₈Ph₈) (**10**; 15 mg) in toluene (5 mL) was refluxed under nitrogen for 90 min, resulting in orange-red precipitates. The solids were filtered, washed with dichloromethane, and dried under vacuum. The product was characterized as [W(C₅Ph₅)₂]_x (**5**; 13 mg, 87%).

Reaction of 10 and Carbon Monoxide. A 100 mL three-necked, round-bottomed flask was equipped with a magnetic stirbar. One neck was stopped, one had a reflux condenser topped with a stopcock connected to an oil bubble, and the third neck had an inlet tube for introduction of carbon monoxide. A solution of W(PhC≡CPh)(η^8 -C₈Ph₈) (**10**; 50 mg, 0.046 mmol) in THF (10 mL) was transferred into the flask and saturated with carbon monoxide gas. With carbon monoxide bubbling through the solution, it was heated at 50 °C for 10 min. The solution was concentrated to ca. 3 mL and subjected to TLC, with dichloromethane/hexane (3:7, v/v) as eluent. The material forming the first, red band afforded W(CO)(PhC≡CPh)(η^5 -C₃Ph₃(C₅Ph₅)) (**3**; 36 mg, 0.032 mmol, 70%). The material forming the second, purple band gave W(CO)(PhC≡CPh)(η^6 -C₃Ph₃(C₅Ph₅)) (**4**; 11 mg, 0.1 mmol, 22%).

Structure Determination for 7. A suitable crystal of W(η^5 -C₅Ph₅)₂(=O) (**7**) with approximate dimensions of 0.33 × 0.35 × 0.40 mm was mounted on a glass fiber and aligned on the diffractometer. Lattice parameters were determined from 18 carefully centered reflections in the range 9.2° < 2θ < 16.7°. On the basis of a statistical analysis of intensity distribution, and successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$ (No. 2). The data were collected at 23 °C with a maximum 2θ value of 47.1°. Scans of width (1.26 + 0.34 tan θ)° were made at a speed of 8.0°/min (in ω). Of the 7981 reflections which were collected, 7586 were unique ($R_{\text{int}} = 0.038$). The intensities of three representative reflections were measured after every 150 reflections; no decay was observed. The linear absorption coefficient, μ, for Mo Kα radiation was 23.1 cm⁻¹. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.78 to 1.00. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods¹⁰ and expanded using Fourier techniques.¹¹ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 5631 observed reflections ($I > 3.00\sigma(I)$) and 649 variable parameters. All calculations were carried out with the TEXSAN crystallographic software package of the Molecular Structure Corp.¹² A summary of relevant crystallographic data is provided in Table 1.

Structure Determination for 10. A suitable crystal of W(PhC≡CPh)(η^8 -C₈Ph₈) (**10**) with approximate dimensions of 0.26 × 0.33 × 0.41 mm was mounted on a glass fiber and aligned on the diffractometer. Lattice parameters were determined from 16 carefully centered reflections in the range 9.5° < 2θ < 14.7°. On the basis of a statistical analysis of intensity distribution, and successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$ (No. 2). The data were collected at 23 °C with a maximum 2θ value of 45.4°. Scans of width (1.42 + 0.34 tan θ)° were made at a speed of 16.0°/min (in ω). Of the 7424 reflections which were collected, 6993 were unique ($R_{\text{int}} = 0.068$). The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards

Table 1. Crystallographic Data for (η^5 -C₅Ph₅)₂W(=O) (7**) and W(PhC≡CPh)(η^8 -C₈Ph₈) (**10**)**

	7	10
chem formula	C ₇₀ H ₅₀ OW	C ₇₀ H ₅₀ W
cryst solvents		1/2 CH ₂ Cl ₂ + 3/2 C ₆ H ₆
fw	1091.01	1234.65
temp, °C	23	23
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	12.663(2)	11.853(3)
b, Å	12.759(3)	13.372(3)
c, Å	18.702(3)	21.584(4)
α, deg	104.55(2)	89.74(2)
β, deg	91.87(2)	87.65(2)
γ, deg	117.64(1)	64.85(2)
V, Å ³	2551(1)	3093(1)
Z	2	2
R ^a	0.034	0.092
R _w ^b	0.030	0.121
GOF	1.59	3.23
D _{calc} , g cm ⁻³	1.420	1.325
λ, Å	0.710 69	0.710 69

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}.$$

decreased by 18% due to solvent loss. A polynomial correction factor was applied to the data to account for this phenomenon. The linear absorption coefficient, μ, for Mo Kα radiation was 20.0 cm⁻¹. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.86 to 1.00. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. Due to the ill nature (solvent loss) of the data, all carbon atoms were refined isotropically. Only the tungsten and chloride atoms (of solvent) were refined anisotropically. Hydrogen atoms were put in at their idealized positions before the last cycle of refinement. The final cycle of full-matrix least-squares refinement was based on 5068 observed reflections ($I > 3.00\sigma(I)$) and 347 variable parameters. The maximum and minimum peaks on the final difference Fourier map corresponded to 5.01 and -2.44 e/Å³, respectively. A summary of relevant crystallographic data is provided in Table 1.

Results and Discussion

Reactions of W(CO)(PhC≡CPh)₃ and W(NCMe)(PhC≡CPh)₃ with Diphenylacetylene. W(CO)(PhC≡CPh)₃ (**1**) shows little reactivity toward diphenylacetylene in refluxing toluene solution. It appears that the W(CO)(RC≡CR')₃ stoichiometry is particularly stable, as suggested by theoretical analyses.¹³ However, under harsher conditions by heating **1** and diphenylacetylene in a sealed tube at 120 °C, reactions involving alkyne-alkyne coupling occur to produce the carbocyclic and metallacyclic complexes W(CO)(PhC≡CPh)₂(η^4 -C₄Ph₄) (**2**; 40%), W(CO)(PhC≡CPh)(η^5 -C₃Ph₃(C₅Ph₅)) (**3**; 13%), and W(CO)(PhC≡CPh)(η^6 -C₃Ph₃(C₅Ph₅)) (**4**; 6%) together with the tungstenocene oligomer [W(C₅Ph₅)₂]_x (**5**) in 32% yield.

Interestingly, replacement of the carbonyl group of **1** by a labile acetonitrile ligand facilitates the coupling reaction, and different products are obtained depending on the ratio of substrates and the reaction conditions, such that treating W(NCMe)(PhC≡CPh)₃ (**8**) with equimolar diphenylacetylene affords W(NCMe)(PhC≡CPh)₂(η^4 -C₄Ph₄) (**9**) in high yield, while a similar reaction in the presence of 2 equiv (or more) of di-

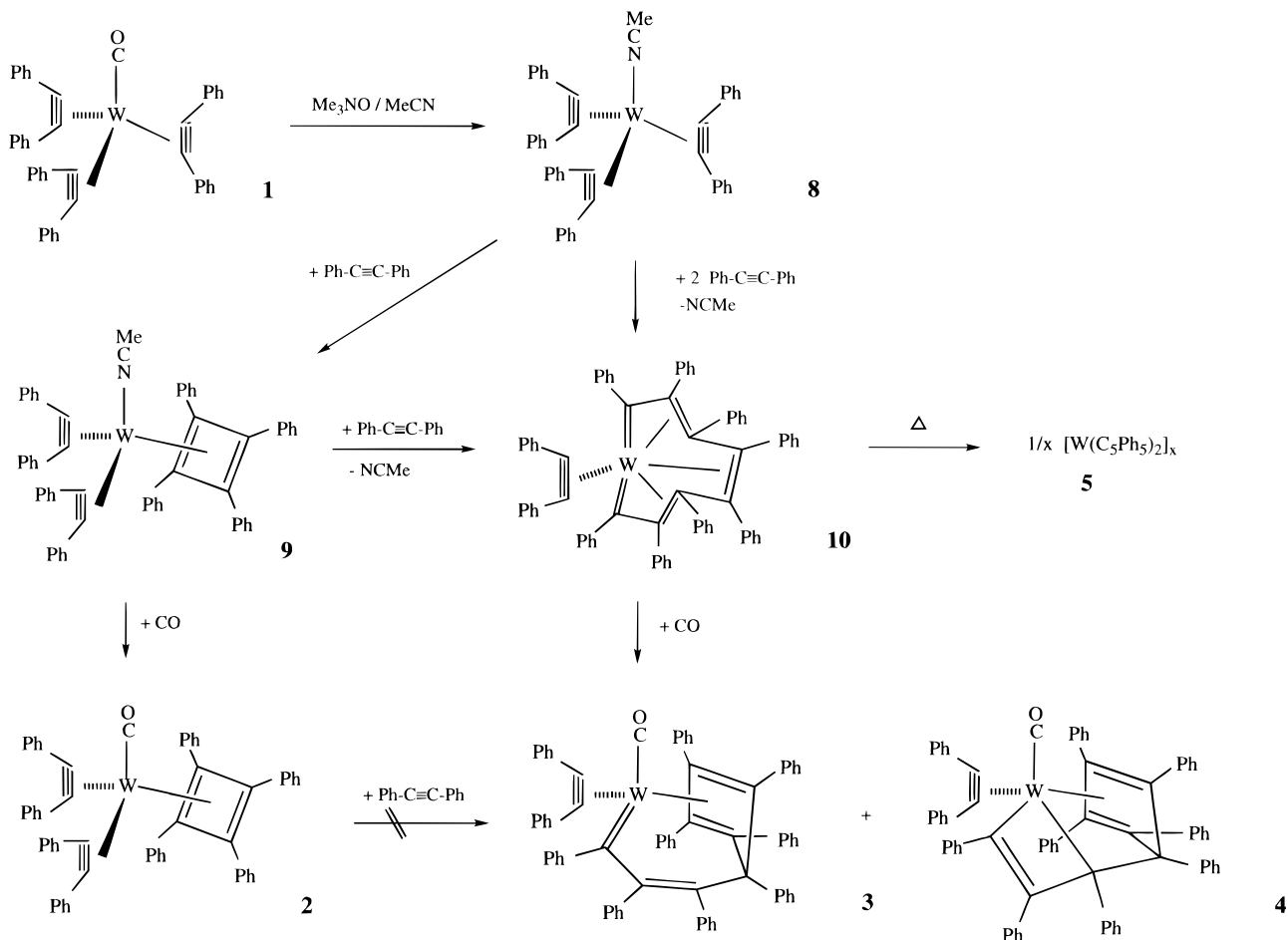
(10) SIR92: Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

(11) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. DIRDIF 94, Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1994.

(12) TEXSAN: Crystal Structure Analysis Package; Molecular Structure Corp., The Woodlands, TX, 1985, 1992.

(13) (a) King, R. B. *Inorg. Chem.* **1968**, *7*, 1044. (b) Wink, D. J.; Greagan, T. *Organometallics* **1990**, *9*, 328.

Scheme 1



phenylacetylene leads to the nine-membered metalla-cyclic complex $W(\text{PhC}\equiv\text{CPh})(\eta^8\text{-C}_8\text{Ph}_8)$ (**10**) as the major product. Reaction of **9** and diphenylacetylene also produces **10**, but in low yield. Compound **10** transforms into **5** upon prolonged standing in hot toluene. However, in the presence of carbon monoxide, complexes **3** and **4** are obtained as the only metal-containing products. The results are summarized in Scheme 1.

Oligomerization of alkynes mediated by transition metals generally leads to cyclobutadiene, arene, and cyclooctatetraene complexes or the corresponding metallocycles.¹⁴ Thus, formation of five-membered cyclopentadiene and cyclopentadienyl derivatives **3**, **4**, and **5** is unique.¹⁵ Compound **10** contains a metallacyclononapentaene unit, which apparently arises from coupling of four diphenylacetylene ligands at the tungsten center. Linking of four alkyne molecules at a dimolybdenum system was previously observed, but a bridging metallacyclononatetraene moiety was formed.¹⁶ It is of interest to note that the skeletal carbons of **10** rearrange to give two cyclopentadienyl groups in **5** instead of releasing a cyclooctatetraene (C_8Ph_8)¹⁷ or a cyclodeca-

pentaene ($\text{C}_{10}\text{Ph}_{10}$) species. In this transformation, mononuclear tungstenocene $W(\text{C}_5\text{Ph}_5)_2$ is likely the reactive intermediate generated in situ.

Characterization of Compounds 2, 3, 4, and 9. Spectroscopic properties of $W(\text{CO})(\text{PhC}\equiv\text{CPh})_2(\eta^4\text{-C}_4\text{Ph}_4)$ (**2**), $W(\text{NCMe})(\text{PhC}\equiv\text{CPh})_2(\eta^4\text{-C}_4\text{Ph}_4)$ (**9**), and $W(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_3\text{Ph}_3(\text{C}_5\text{Ph}_5))$ (**3**) were briefly described in previous communications,^{3,4} and the structures of **2** and **3** were established by X-ray diffraction studies.

If we take the centers of the alkyne and cyclobutadiene ligands, the geometry of **2** and **9** can be viewed as a distorted tetrahedron. The terminal CO (or NCMe) and η^4 -cyclobutadiene ligands are normally counted as two- and four-electron donors, respectively; thus, the remaining two alkyne ligands must provide six electrons to the neutral tungsten atom to satisfy the 18-electron rule.¹⁸ Since the two alkyne ligands are equivalent, as evidenced by equal $\text{C}\equiv\text{C}$ bond lengths and ^{13}C chemical shifts, the actual structure is best regarded as a resonance hybrid with two canonical forms involving one four-electron-donor ($\pi_{\parallel} + \pi_{\perp}$) and one two-electron-donor (π_{\parallel}) alkyne ligand. Rotation of alkyne ligands is slow on the NMR time scale, thus displaying two ^{13}C resonances for the $\text{C}\equiv\text{C}$ carbons, whereas the cyclobutadiene ligand is fluxional with facial ring rotation and only one ^{13}C resonance is observed down to -50°C .

Compound **3** contains a terminal CO, a diphenylacetylene, and a cyclopentadienylpropenylidene ($=\text{CPh}$ -

(14) (a) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081 and references therein. (b) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1.

(15) Reinheimer, H.; Moffat, J.; Maitlis, P. M. *J. Am. Chem. Soc.* **1970**, *92*, 2285.

(16) (a) Green, M.; Norman, N. C.; Orpen, A. G. *J. Am. Chem. Soc.* **1981**, *103*, 1269. (b) Connelly, N. G.; Metz, B.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1994**, 2109. (c) Bott, S. G.; Brammer, L.; Connelly, N. G.; Green, M.; Orpen, A. G.; Paxton, J. F.; Schaverien, C. J. *J. Chem. Soc., Dalton Trans.* **1990**, 1957.

(17) Colborn, R. E.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 5470.

(18) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988.

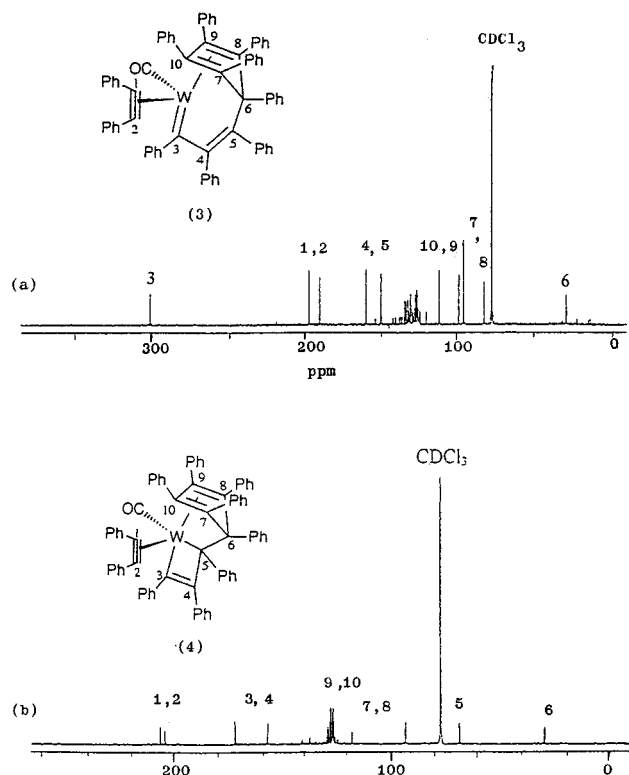


Figure 1. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the ^{13}C -enriched compounds (a) $\text{W}(\text{CO})(\text{Ph}^*\text{C}\equiv\text{CPh})(\eta^5\text{-}^*\text{C}_3\text{Ph}_3(^*\text{C}_5\text{Ph}_5))$ (**3***) and (b) $\text{W}(\text{CO})(\text{Ph}^*\text{C}\equiv\text{CPh})(\eta^5\text{-}^*\text{C}_3\text{Ph}_3(^*\text{C}_5\text{Ph}_5))$ (**4***), obtained from the reaction of $\text{W}(\text{CO})(\text{Ph}^*\text{C}\equiv\text{CPh})_3$ and $\text{Ph}^*\text{C}\equiv\text{CPh}$ (ca. 10% ^{13}C).

$\text{CPh}=\text{CPhC}_5\text{Ph}_5$) ligand, with each group formally donating two, four, and six electrons, respectively, to the neutral tungsten atom. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3***, obtained from reaction of $\text{W}(\text{CO})(\text{Ph}^*\text{C}\equiv\text{CPh})_3$ and $\text{Ph}^*\text{C}\equiv\text{CPh}$ (each ca. 10% ^{13}C), is shown in Figure 1a. The downfield signal at δ 300.8 is assigned to the alkylidene carbon.¹⁹ The signals at δ 197.4 and 190.0 are assigned to the $\equiv\text{CPh}$ resonances, which are characteristic of four-electron-donor alkyne ligands.²⁰ The signals at δ 159.7 and 150.3 are comparable with those of free alkenes and are assigned to the two uncoordinated allyl carbons. The remaining four resonances ranging from δ 111.8 to 81.9, and an upfield signal at δ 29.7, are assigned to the butadiene carbons and the sp^3 -hybrid carbon of the cyclopentadienyl group, respectively.

$\text{W}(\text{CO})(\text{PhC}\equiv\text{CPh})(\eta^5\text{-C}_3\text{Ph}_3(\text{C}_5\text{Ph}_5))$ (**4**) forms air-stable, purple solids. The FAB mass spectrum shows the molecular ion at m/z 1102 for ^{184}W and fragments resulting from successive loss of a CO and a diphenylacetylene. We were not able to obtain crystals suitable for an X-ray diffraction study. However, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4*** (Figure 1b) shows great resemblance to that of **3***, indicating that their structures might be closely related. Since compound **4** reveals no alkylidene carbon resonance and an additional upfield resonance at δ 68.0 is observed, the propenylidene moiety of **3** probably appears as a metallacyclobutene ring for **4**. We have tried to interconvert compounds **3** and **4** thermally, but this leads to no reaction.

(19) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: New York, 1981.

(20) (a) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1. (b) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.

Characterization of 10. $\text{W}(\text{PhC}\equiv\text{CPh})(\eta^8\text{-C}_8\text{Ph}_8)$ (**10**) is an air-stable, dark red, crystalline solid. The FAB mass spectrum presents the molecular ion at m/z 1074 for ^{184}W plus an ion corresponding to loss of a diphenylacetylene. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the ^{13}C -enriched complex $\text{W}(\text{Ph}^*\text{C}\equiv\text{CPh})(\eta^8\text{-}^*\text{C}_8\text{Ph}_8)$ (**10''**) is illustrated in Figure 2b. The two resonances at δ 196.8 and 189.5 are assigned to the alkyne carbons. The C_8Ph_8 skeletal carbons give rise to only four resonance signals, implying a plane of symmetry passing through the molecule. The low field resonance at δ 240.3 with ^{183}W satellites ($^1J_{\text{W-C}} = 96$ Hz) is characteristic of alkylidene type carbons,^{19,21} while the remaining signals at δ 130.0, 126.5, and 93.5 are in the range for alkene carbons coordinated to transition metals. Due to the absence of diagnostic spectral features to reveal the structure, a single-crystal X-ray diffraction study was performed.

Crystal Structure of 10. An ORTEP drawing of **10** is shown in Figure 4, where the phenyl groups have been artificially omitted for clarity. Selected bond distances and bond angles are given in Table 2. There are one and a half benzene molecules and a half dichloromethane molecule cocrystallized with each tungsten complex in the asymmetric unit cell. Compound **10** consists of a central tungsten atom bonded to one diphenylacetylene and one octaphenyltetraene group. Although the molecule has no crystallographically imposed symmetry in the solid state, it exhibits the expected idealized C_s symmetry in solution, as evidenced by ^{13}C NMR.

The $\text{W}(\eta^8\text{-C}_8\text{Ph}_8)$ moiety forms a metallacycle. It appears to have tungsten-carbon double bonds at both ends ($\text{W1-C3} = 2.01(2)$ Å and $\text{W1-C10} = 2.03(2)$ Å), and π -donation from the triene unit (C4-C9) to the tungsten atom. The atoms W1, C3, C4, and C23 are coplanar to within $\pm 0.05(2)$ Å and the W1, C9, C10, and C65 atoms to within $\pm 0.04(2)$ Å; the dihedral angle between the two planes is 20.5° . Furthermore, the angles $\angle\text{C4-C3-C23} = 123(1)^\circ$ and $\angle\text{C9-C10-C65} = 125(1)^\circ$ are consistent with the expected value for sp^2 -hybridized alkylidene carbons. The W-C distances to the triene linkage (C4-C9) are variable, such that the two terminal alkenes are bonded to the tungsten atom asymmetrically, with $\text{W1-C4} = 2.48(2)$ Å and $\text{W1-C9} = 2.46(2)$ Å being significantly longer than $\text{W1-C5} = 2.25(2)$ Å and $\text{W1-C8} = 2.23(2)$ Å, while the W-C distances to the internal alkene carbons, C6 and C7, are equal, being $2.38(2)$ Å. The C4, C5, C29, and C35 atoms, the C5, C6, C7, C8, C41, and C53 atoms, and the C8, C9, C47, and C59 atoms are also coplanar.

The diphenylacetylene carbons are bonded to the tungsten atom equally. The W1-C1 , W1-C2 , and C1-C2 distances are $2.09(2)$, $2.10(2)$, and $1.31(3)$ Å, respectively. The phenyl groups are bent away from the $\text{C}\equiv\text{C}$ axis by angles averaging $46(2)^\circ$. The dihedral angles between the plane of the alkyne moiety (W1, C1, and C2) and the planes of alkylidene moieties (W1, C3, C23) and (W1, C10, C65) are 69.7 and 74.7° , respectively.

Characterization of 5. Solid $[\text{W}(\text{C}_5\text{Ph}_5)_2]_x$ (**5**) is thermally robust to 350°C . It presents essentially no solubility to all common solvents. Thus, characterization is based on elemental analyses, IR and mass

(21) Yeh, W.-Y.; Peng, S.-M.; Liu, L.-K. *Inorg. Chem.* **1993**, *32*, 2965.

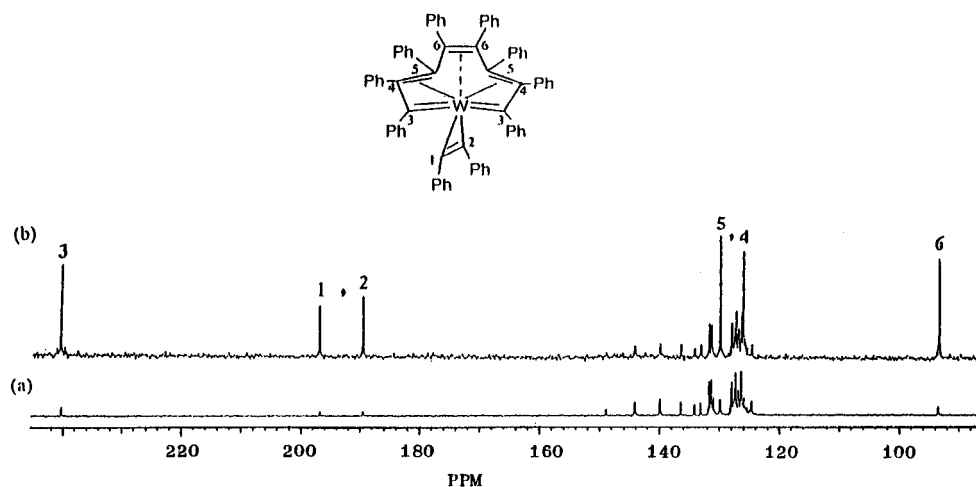


Figure 2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of (a) $\text{W}(\text{PhC}\equiv\text{CPh})(\eta^8\text{-C}_8\text{Ph}_8)$ (**10**) and (b) ^{13}C -enriched $\text{W}(\text{Ph}^*\text{C}\equiv\text{CPh})(\eta^8\text{-}^*\text{C}_8\text{Ph}_8)$ (**10''**), obtained from the reaction of $\text{W}(\text{NCMe})(\text{Ph}^*\text{C}\equiv\text{CPh})_3$ and 2 equiv of $\text{Ph}^*\text{C}\equiv\text{CPh}$ (ca. 10% ^{13}C).

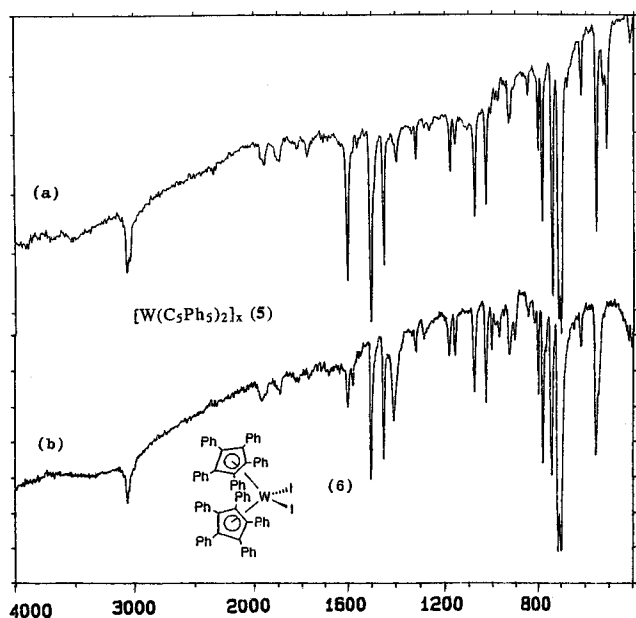


Figure 3. IR spectra of (a) $[\text{W}(\text{C}_5\text{Ph}_5)_2]_x$ (**5**) and (b) $\text{W}(\eta^5\text{-C}_5\text{Ph}_5)_2(\text{I})_2$ (**6**) in KBr pellets.

spectroscopy, and its reaction with I_2 to give $\text{W}(\eta^5\text{-C}_5\text{Ph}_5)_2(\text{I})_2$ (**6**).

The IR spectrum of **5** (Figure 3a) is very similar to that of **6** (Figure 3b), suggesting an η^5 -bonding mode for the C_5Ph_5 groups of **5**. In addition, the absence of strong W–H stretching bands²² in the region 2000–1700 cm^{-1} could preclude a dihydrido formula, $\text{W}(\text{C}_5\text{Ph}_5)_2(\text{H})_2$, for **5**. The EI mass spectrum of **5**, obtained at 350 °C and 70 eV, displays the highest ion peak at m/z 1074 for ^{184}W , corresponding to the mononuclear tungstenocene $\text{W}(\text{C}_5\text{Ph}_5)_2$. Thus, it is likely that compound **5** persists a dimeric or trimeric structure with a regular $\text{W}(\eta^5\text{-C}_5\text{Ph}_5)_2$ unit.

The simple mononuclear complex MCp_2 ($\text{M} = \text{Mo}$, W),²³ analogous to chromocene,²⁴ is unstable. All attempts to prepare it and its analogues containing alkyl- and arylcyclopentadienyls have led to isolation of poly-

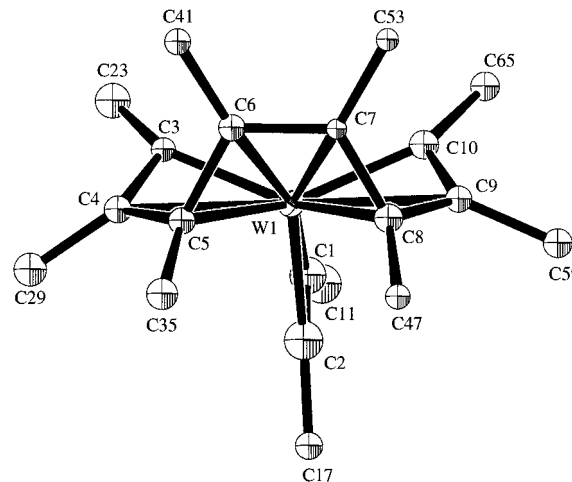


Figure 4. Molecular structure of $\text{W}(\text{PhC}\equiv\text{CPh})(\eta^8\text{-C}_8\text{Ph}_8)$ (**10**). The phenyl groups have been artificially omitted, except the *ipso* carbon atoms, for clarity.

nuclear products.²⁵ $\text{Mo}(\eta^5\text{-C}_5\text{Ph}_5)_2$ was previously isolated as a side product from the reaction of $\text{PhC}\equiv\text{CPh}$ with either $\text{Mo}(\text{CO})_6$ or $\text{Mo}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_5\text{Me})$,²⁶ with not very extensive characterization; this complex is practically insoluble in all common solvents and is presumably also polymeric.

Preparation and Characterization of 6 and 7. Heating solid $[\text{W}(\text{C}_5\text{Ph}_5)_2]_x$ (**5**) and I_2 in benzene affords a dark green powder, which is recrystallized from dichloromethane/benzene to yield essentially pure $\text{W}(\eta^5\text{-C}_5\text{Ph}_5)_2(\text{I})_2$ (**6**). It appears that diiodine undergoes an oxidative-addition reaction at the tungsten center, leading to cleavage of the oligomer (presumably breaking tungsten–tungsten bonds). Subsequent treatment of **6** with AgBF_4 in wet dichloromethane solution affords the oxo complex $\text{W}(\eta^5\text{-C}_5\text{Ph}_5)_2(=\text{O})$ (**7**) in good yield (eq 1). Analogous group 6 “bent metallocene” MCp_2X_2 can be prepared by stirring the corresponding dihydrides in CHCl_3 or other appropriate halogenating agent.^{22a,27}

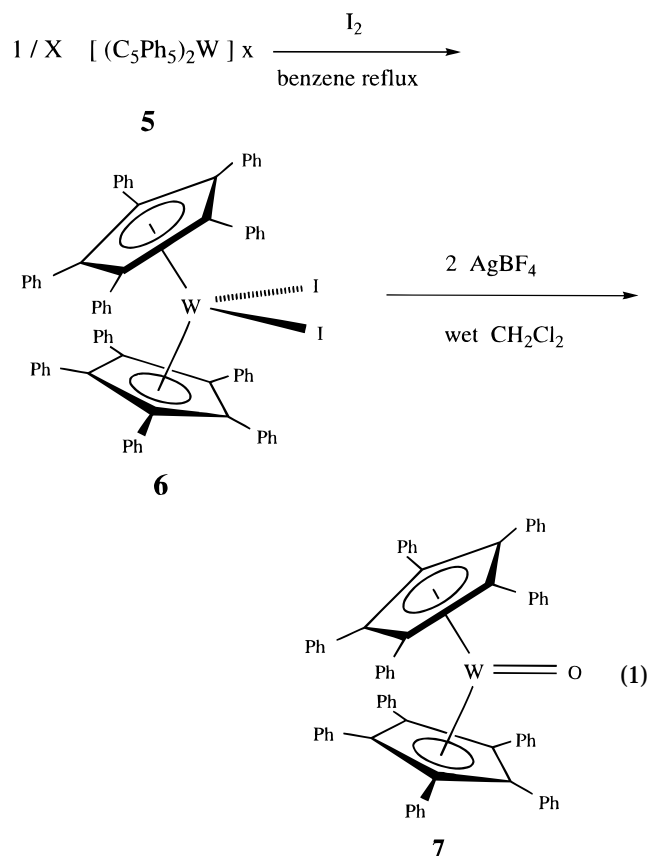
(22) (a) Dub, M. *Organometallic Compounds*, 2nd ed.; Springer-Verlag: Berlin, 1966; Vol. 1. (b) Girling, R. B.; Grebenik, P.; Perutz, R. N. *Inorg. Chem.* **1986**, *25*, 31.

(23) Grebenik, P.; Downs, A. J.; Green, M. L. H.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1979**, 742.

(24) (a) Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882. (b) O'Hare, D.; Murphy, V. J.; Kaltsoyannis, N. *J. Chem. Soc., Dalton Trans.* **1993**, 383. (c) Castellani, M. P.; Geib, S. J.; Rheingold, A. L.; Troglor, W. C. *Organometallics* **1987**, *6*, 1703.

(25) (a) Thomas, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 1838. (b) Thomas, J. L.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1386.

(26) Hübel, W.; Merényi, R. *J. Organomet. Chem.* **1964**, *2*, 213.



Reduction of $WCp'Cl_4(PMe_3)$ ($Cp' = C_5Me_5$) with magnesium and reaction with $LiCp'$ also provides a convenient route to $W(Cp')_2(Cl)_2$, from which a range of other derivatives can be prepared.²⁸ For example, the oxo complexes $MCp'_2(=O)$ were synthesized by treating MCp'_2Cl_2 with aqueous KOH.²⁸

$W(\eta^5-C_5Ph_5)_2(I)_2$ (**6**) forms an air-stable, dark green crystalline solid. It decomposes readily in solution. Compound **6** gives satisfactory C, H microanalyses, though the FAB mass spectrum displays the highest mass at m/z 1074, corresponding to the $M^+ - 2I$ fragment. The oxo complex $W(\eta^5-C_5Ph_5)_2(=O)$ (**7**) also forms air-stable, dark green crystals. The FAB mass spectrum of **7** gives the parent ion at m/z 1090 and an ion at m/z 1074 for loss of an oxygen atom. The tungsten-oxygen double bond is characterized by a strong $\nu(W=O)$ band in its IR spectrum at 906 cm^{-1} , which is comparable with those recorded for $W(\eta^5-C_5Me_5)_2(=O)$ (860 cm^{-1})²⁹ and $W(\eta^5-C_5Me_5)(\eta^1-C_5Me_5)(=O)_2$ (895 and 935 cm^{-1}).³⁰ Apparently, the tungsten center of **7** persists in a closed-shell configuration ($18e^-$) without oxygen lone-pair donation; otherwise, an absorption in the range $930\text{--}1000\text{ cm}^{-1}$ would be observed for the more common $-W=O^+$ bonding mode.³¹

Crystal Structure of 7. An ORTEP drawing of $W(\eta^5-C_5Ph_5)_2(=O)$ (**7**) is shown in Figure 5. Selected

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) of $W(PhC\equiv CPh)(\eta^8-C_8Ph_8)$ (10**)**

Distances			
W1-C1	2.09(2)	W1-C2	2.10(2)
W1-C3	2.01(2)	W1-C4	2.48(2)
W1-C5	2.25(2)	W1-C6	2.39(2)
W1-C7	2.38(2)	W1-C8	2.23(2)
W1-C9	2.46(2)	W1-C10	2.03(2)
C1-C2	1.31(3)	C1-C11	1.47(3)
C2-C17	1.47(3)	C3-C4	1.43(3)
C3-C23	1.42(3)	C4-C5	1.46(3)
C4-C29	1.50(3)	C5-C6	1.52(3)
C5-C35	1.46(3)	C6-C7	1.46(3)
C6-C41	1.47(3)	C7-C8	1.48(3)
C7-C53	1.47(3)	C8-C9	1.38(3)
C8-C47	1.50(3)	C9-C10	1.36(3)
C9-C59	1.51(3)	C10-C65	1.51(3)
Angles			
C1-W1-C2	36.4(9)	C1-W1-C3	94.2(9)
C1-W1-C4	105.3(8)	C1-W1-C5	130.7(8)
C1-W1-C6	165.5(8)	C1-W1-C7	158.7(8)
C1-W1-C8	125.4(8)	C1-W1-C9	101.7(8)
C1-W1-C10	90.9(9)	C2-W1-C3	108.6(9)
C2-W1-C4	97.7(8)	C2-W1-C5	104.9(8)
C2-W1-C6	140.9(8)	C2-W1-C7	137.6(8)
C2-W1-C8	101.4(8)	C2-W1-C9	95.1(8)
C2-W1-C10	105.2(9)	C1-C2-C17	136(2)
C2-C1-C11	131(2)	W1-C1-C2	72(1)
W1-C2-C1	71(1)	W1-C3-C4	90(1)
W1-C3-C23	142(1)	C4-C3-C23	123(1)
W1-C4-C3	54(1)	W1-C4-C5	63(1)
W1-C4-C29	142(1)	C3-C4-C5	108(1)
C3-C4-C29	127(1)	C5-C4-C29	122(1)
W1-C5-C4	80(1)	W1-C5-C6	75(1)
W1-C5-C35	135(1)	C4-C5-C6	110(1)
C4-C5-C35	120(1)	C6-C5-C35	121(1)
W1-C6-C5	66(1)	W1-C6-C7	71(1)
W1-C6-C41	139(1)	C5-C6-C7	117(1)
C5-C6-C41	121(1)	C7-C6-C41	120(1)
W1-C7-C6	72(1)	W1-C7-C8	66(1)
W1-C7-C53	131(1)	C6-C7-C8	119(1)
C6-C7-C53	119(1)	C8-C7-C53	120(1)
W1-C8-C7	76(1)	W1-C8-C9	82(1)
W1-C8-C47	131(1)	C7-C8-C9	107(1)
C7-C8-C47	121(1)	C9-C8-C47	123(1)
W1-C9-C8	64(1)	W1-C9-C10	55(1)
W1-C9-C59	147(1)	C8-C9-C10	112(2)
C8-C9-C59	125(1)	C10-C9-C59	122(1)
W1-C10-C9	90(1)	W1-C10-C65	141(1)
C9-C10-C65	125(2)		

bond distances and bond angles are given in Table 3. The unit cell consists of two molecules related by inversion center symmetry. Each molecule has a formally W(IV) atom surrounded by two pentaphenylcyclopentadienyl groups and an oxo ligand. The overall geometry can be viewed as a bent sandwich where the two cyclopentadienyl groups are splayed with respect to the oxo ligand, with an interplanar angle of 26° . Ignoring the phenyl groups, the molecule has an approximate C_s symmetry with a mirror plane passing through the W1, O1, C7, and C47 atoms and the middle point of the C1-C2 bond. The tungsten atom is not situated right behind the centroid of the two cyclopentadienyl rings. Its projection point is 0.26 \AA away from the centroid of the C1-C5 ring, leaning toward the C1-C2 edge, and 0.39 \AA away from the centroid of the C6-C10 ring, leaning toward the C7 atom. There appears to be considerable steric repulsions between the two C_5Ph_5 moieties such that the cyclopentadienyl groups are staggered. The phenyl groups are canted to each cyclopentadienyl ring in a paddlewheel fashion. The phenyl groups on the cyclopentadienyl rings are displaced outward from the tungsten atom.

(27) Davis, R.; Kane-Maguire, L. A. P. in *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, U.K., 1982; Vol. 3, p 1321, and references therein.

(28) Parkin, G.; Bercaw, J. E. *Polyhedron* **1988**, *7*, 2053.

(29) Parkin, G.; Bercaw, J. E. *J. Am. Chem. Soc.* **1989**, *111*, 391.

(30) Parkin, G.; Marsh, R. E.; Schaefer, W. P.; Bercaw, J. E. *Inorg. Chem.* **1988**, *27*, 3262.

(31) (a) Herrmann, W. A.; Serrano, R.; Bock, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 383. (b) Besecker, C. J.; Klemperer, W. G. *J. Am. Chem. Soc.* **1980**, *102*, 7598. (c) Day, V. W.; Fredrich, M. F.; Thompson, M. R.; Klemperer, W. G.; Liu, R.-S.; Shum, W. *J. Am. Chem. Soc.* **1981**, *103*, 3597.

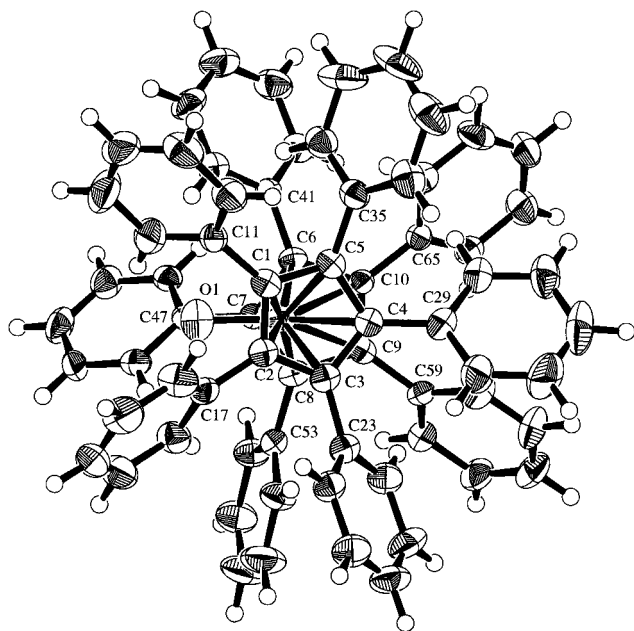


Figure 5. Molecular structure of $W(\eta^5\text{-C}_5\text{Ph}_5)_2(=\text{O})$ (**7**).

The W1–O1 distance of 1.714(4) Å is typical for a tungsten–oxygen double bond. The interesting feature of the two $\eta^5\text{-C}_5\text{Ph}_5$ groups is that they show unusual π -coordination to the tungsten atom and are more aptly described as asymmetric $\eta^3\text{-allyl}/\eta^2\text{-olefin}$ -type ligands (Figure 6). In the C1–C5 ring, the atoms C1, C2, C3, and C5 are coplanar to within 0.002(6) Å and only the C4 atom is displaced from the plane, away from W1, by 0.1 Å; this gives a dihedral angle of 6.6° between the olefinic plane C1, C2, C3, C5 and the allylic plane C3, C4, C5. Among all W–C_{ring} bond distances, the W1–C1 and W2–C2 distances (2.527(6) and 2.495(6) Å) are significantly longer than those to the allylic carbon atoms C3, C4, and C5 (2.421(6), 2.476(6), and 2.460(6) Å, respectively). The C_{ring}–C_{ring} distances are varied. They range from 1.435(8) to 1.451(8) Å with the C1–C2 length of 1.416(8) Å being the shortest. The *ipso* carbon atoms C11 and C17 of the phenyl rings are essentially on the olefin plane, whereas the *ipso* atoms C23, C29, and C35 are displaced away from the allyl plane (C3–C5) by 9.8(6), 9.5(6), and 9.4(6)°, respectively.

The bent $\eta^3:\eta^2$ -bonding mode of the cyclopentadienyl ligand is unambiguously substantiated by the C6–C10 ring. It appears as an opened envelope with the allyl fragment (C6, C7, C8, C47) and olefin fragment (C6, C10, C9, C8) being planar to within 0.002(6) and 0.003(6) Å, respectively, and the dihedral angle between the two planes is 10.4(6)°. The bonding of C6, C7, and C8 atoms is typical of $\eta^3\text{-allyl}$: the central carbon (W1–C7 = 2.322(6) Å) is ca. 0.04 Å closer to the metal than the end carbons (W1–C6 = 2.355(6) Å and W1–C8 = 2.374(6) Å). The W–C distances to the olefinic carbon atoms C9 and C10 are substantially longer, being 2.646(6) and 2.618(6) Å. There appears to be a considerable localized feature of the ring bonds, such that the C9–C10 length (1.402(8) Å) is ca. 0.06 Å shorter than the lengths of C6–C10 and C8–C9 (1.463(8) and 1.467(8) Å) and is ca. 0.04 Å shorter than the lengths of C6–C7 and C7–C8 (1.440(8) Å). The phenyl *ipso* carbon atoms C41 and C53 are bent outward from the allyl plane (away from W1) by 5.8(6) and 10.4(6)°. The

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $(\eta^5\text{-C}_5\text{Ph}_5)_2\text{W}(=\text{O})$ (**7**)

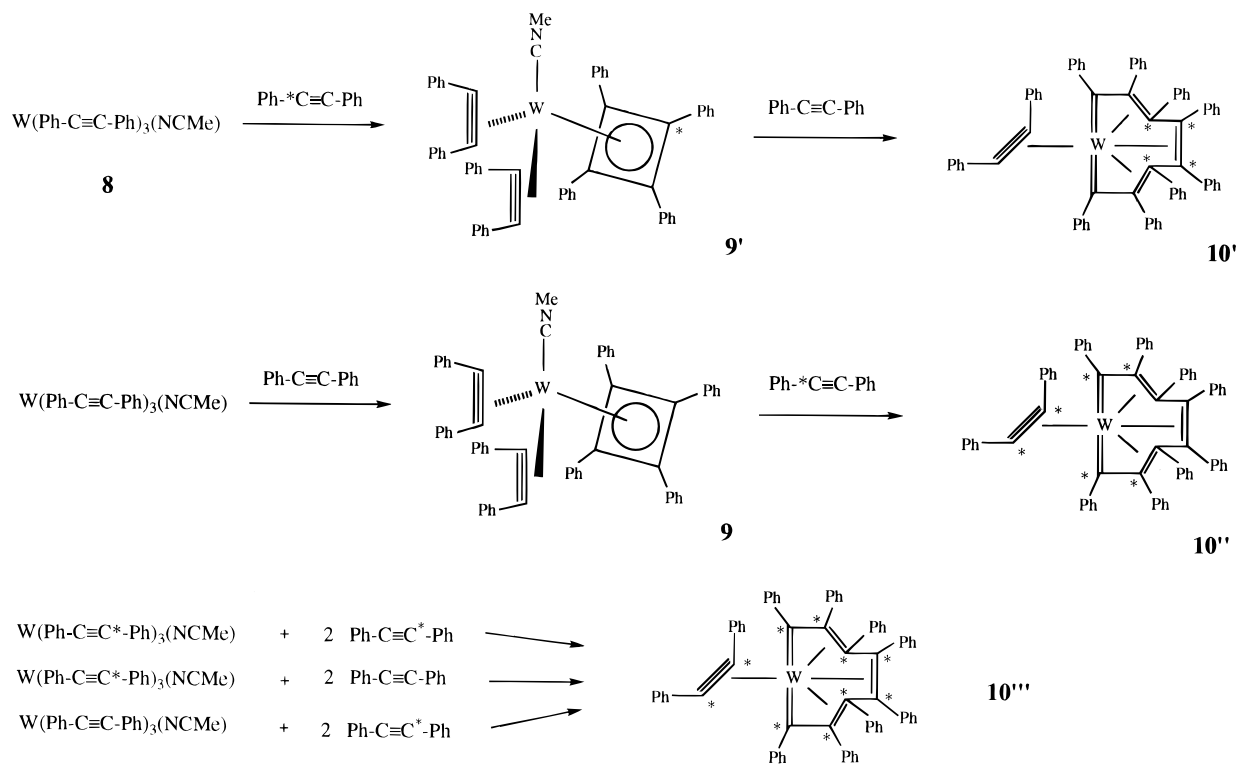
Distances			
W1–O1	1.714(4)	W1–C1	2.527(6)
W1–C2	2.494(6)	W1–C3	2.421(6)
W1–C4	2.476(6)	W1–C5	2.460(6)
W1–C6	2.355(6)	W1–C7	2.322(6)
W1–C8	2.374(6)	W1–C9	2.646(6)
W1–C10	2.618(6)	C1–C2	1.416(8)
C1–C5	1.449(8)	C1–C11	1.498(8)
C2–C3	1.435(8)	C2–C17	1.488(8)
C3–C4	1.451(8)	C3–C23	1.486(8)
C4–C5	1.437(8)	C4–C29	1.475(8)
C5–C35	1.504(8)	C6–C7	1.440(8)
C6–C10	1.463(8)	C6–C41	1.504(8)
C7–C8	1.440(8)	C7–C47	1.501(8)
C8–C9	1.467(8)	C8–C53	1.504(8)
C9–C10	1.402(8)	C9–C59	1.485(8)
C10–C65	1.498(8)		
Angles			
O1–W1–C1	80.4(2)	O1–W1–C2	78.3(2)
O1–W1–C3	108.4(2)	O1–W1–C4	132.7(2)
O1–W1–C5	112.0(2)	O1–W1–C6	98.6(2)
O1–W1–C7	78.6(2)	O1–W1–C8	98.1(2)
O1–W1–C9	130.6(2)	O1–W1–C10	131.1(2)
C1–W1–C2	32.7(2)	C1–W1–C5	33.7(2)
C2–W1–C3	33.9(2)	C3–W1–C4	34.4(2)
C4–W1–C5	33.8(2)	C6–W1–C7	35.8(2)
C6–W1–C10	33.7(2)	C7–W1–C8	35.7(2)
C8–W1–C9	33.4(2)	C9–W1–C10	30.9(2)
W1–C1–C2	72.3(4)	W1–C1–C5	70.6(3)
W1–C1–C11	124.7(4)	C2–C1–C5	108.0(6)
C2–C1–C11	126.8(6)	C5–C1–C11	125.1(6)
W1–C2–C1	74.9(4)	W1–C2–C3	70.2(4)
W1–C2–C17	122.0(4)	C1–C2–C3	109.2(6)
C1–C2–C17	123.8(6)	C3–C2–C17	127.0(6)
W1–C3–C2	75.9(4)	W1–C3–C4	74.9(4)
W1–C3–C23	128.1(4)	C2–C3–C4	107.0(6)
C2–C3–C23	124.3(6)	C4–C3–C23	126.6(6)
W1–C4–C29	132.2(4)	W1–C4–C3	70.7(3)
W1–C4–C5	72.4(4)	C3–C4–C5	107.9(6)
C3–C4–C29	126.9(6)	C5–C4–C29	124.0(6)
W1–C5–C1	75.7(4)	W1–C5–C4	73.7(4)
W1–C5–C35	128.8(4)	C1–C5–C4	107.4(6)
C1–C5–C35	121.5(6)	C4–C5–C35	129.1(6)
W1–C6–C7	70.8(3)	W1–C6–C10	83.0(4)
W1–C6–C41	124.6(4)	C7–C6–C10	106.3(5)
C7–C6–C41	123.2(6)	C10–C6–C41	128.2(6)
W1–C7–C6	73.3(4)	W1–C7–C8	74.1(4)
W1–C7–C47	124.7(4)	C6–C7–C8	108.4(5)
C6–C7–C47	126.9(6)	C8–C7–C47	124.2(6)
W1–C8–C7	70.2(4)	W1–C8–C9	83.5(4)
W1–C8–C53	129.1(4)	C7–C8–C9	107.0(5)
C7–C8–C53	124.5(6)	C9–C8–C53	124.8(6)
W1–C9–C8	63.1(3)	W1–C9–C10	73.4(4)
W1–C9–C59	137.8(4)	C8–C9–C10	107.8(6)
C8–C9–C59	124.0(6)	C10–C9–C59	127.0(6)
W1–C10–C6	63.3(3)	W1–C10–C9	75.7(4)
W1–C10–C65	135.5(4)	C6–C10–C9	109.4(5)
C6–C10–C65	122.5(5)	C9–C10–C65	127.2(6)

atoms C59 and C65 are bent away from the olefin plane by 12.5(6) and 10.6(6)°, respectively.

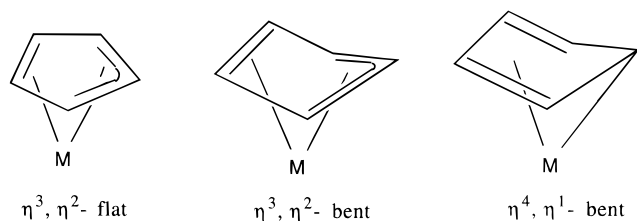
The structure of the analogous complex $\text{Mo}(\eta^5\text{-MeCp})_2(=\text{O})$ was previously described,³² whereas the MeCp rings are essentially flat, with no indication of a “localized” fashion. Thus, the occurrence of an $\eta^3:\eta^2$ -bonding mode for the C_5Ph_5 ligands in **7** is probably due to strong steric repulsions between the phenyl groups. A flat $\eta^3\text{-allyl}/\eta^2\text{-olefin}$ -type coordination has been observed for the pentamethylcyclopentadienyl rings of $\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{Cl})_2(=\text{O})$, $\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{I})_2(=\text{O})$, and $\text{Re}(\eta^5\text{-C}_5\text{Me}_5)(\text{CH}_3)_2(=\text{O})$.³³ Another example of asymmetric ring

(32) Silavwe, N. D.; Chiang, M. Y.; Tyler, D. R. *Inorg. Chem.* **1985**, *24*, 4219.

Scheme 2



configuration is provided by $(\eta^5\text{-C}_5\text{Me}_5)\text{W}(=\text{O})_2(\text{OC}_5\text{-Me}_5)$,³⁰ in which the $\text{W}-(\eta^5\text{-C}_5\text{Me}_5)$ interaction is a mixture of η^5 and η^1 bonding and the ligand is better described as an $\eta^4:\eta^1$ fashion.



Mechanistic Study of the Alkyne–Alkyne Coupling Reaction. The harsh reaction conditions required for $\text{W}(\text{CO})(\text{PhC}\equiv\text{CPh})_3$ (**1**) disables detailed mechanistic study. Thus, C-13 labeling experiments were only performed on $\text{W}(\text{NCMe})(\text{PhC}\equiv\text{CPh})_3$ (**8**). The results, analyzed by ^{13}C NMR spectroscopy, are displayed in Scheme 2. It is found that treating **8** with equimolar $\text{Ph}^*\text{C}\equiv\text{CPh}$ (the asterisk indicates the positions of the ^{13}C label) leads to $\text{W}(\text{NCMe})(\text{PhC}\equiv\text{CPh})_2(\eta^4\text{-}^*\text{CC}_3\text{Ph}_4)$ (**9**), where the ^{13}C label is located exclusively at the cyclobutadiene fragment. Succeeding reaction of **9** and $\text{PhC}\equiv\text{CPh}$ affords **10'**, showing the ^{13}C label in the γ -, δ -positions of the metallacycle. Similar reaction of **9** and $\text{Ph}^*\text{C}\equiv\text{CPh}$ produces **10''**, with the ^{13}C label in the alkyne ligand and α -, β -positions of the metallacycle. However, direct treatments of $\text{W}(\text{NCMe})(\text{PhC}\equiv\text{CPh})_3$ (**8**) with 2 equiv of $\text{Ph}^*\text{C}\equiv\text{CPh}$ or of $\text{W}(\text{NCMe})(\text{Ph}^*\text{C}\equiv\text{CPh})_3$ (**8**) with 2 equiv of $\text{PhC}\equiv\text{CPh}$ or $\text{Ph}^*\text{C}\equiv\text{CPh}$ yield essentially identical results (**10'''**), in which the ^{13}C label scrambles over the alkyne ligand and all the metallacyclic positions.

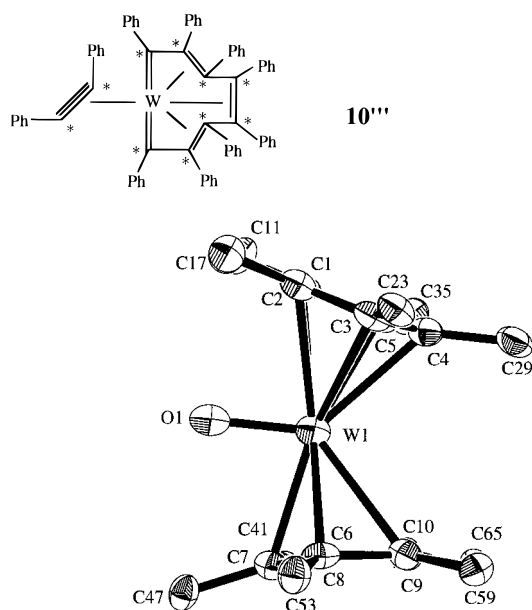
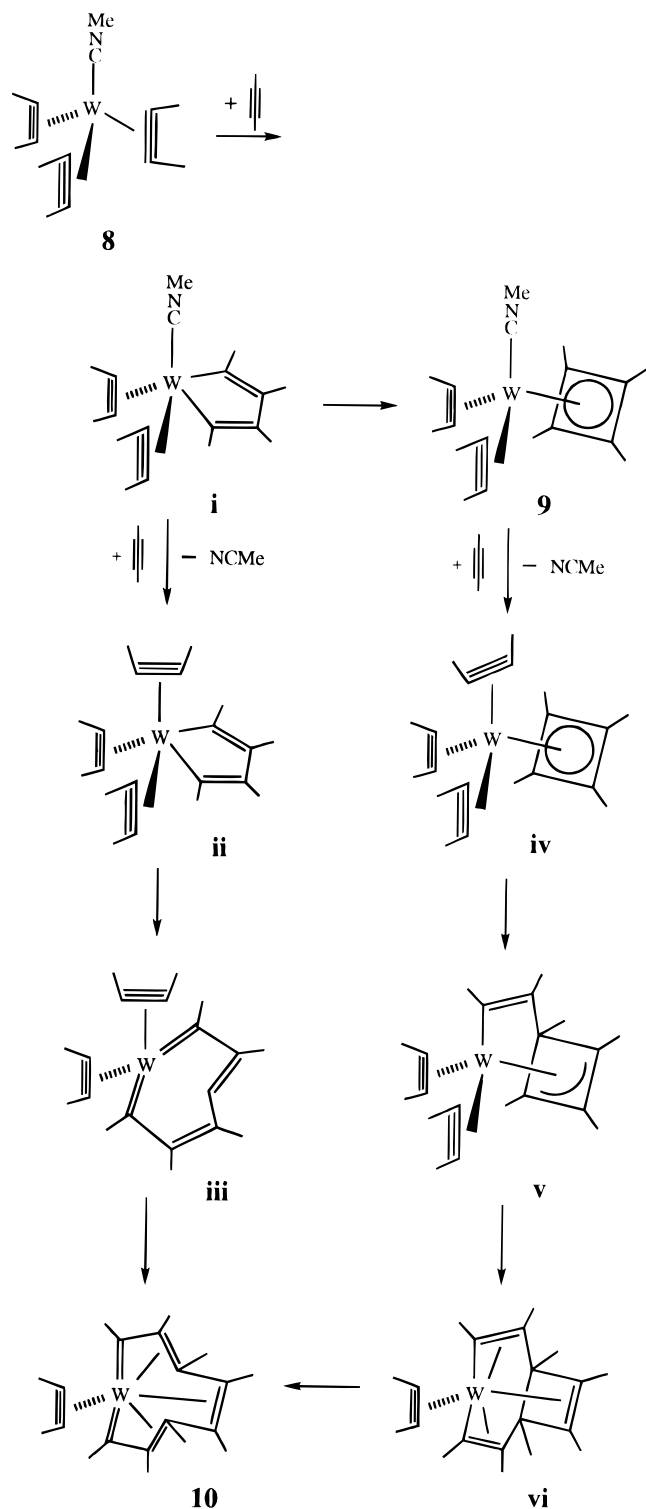


Figure 6. Another view of $\text{W}(\eta^5\text{-C}_5\text{Ph}_5)_2(=\text{O})$ (**7**), showing the bent configuration for the cyclopentadienyl rings. The phenyl groups have been artificially omitted for clarity.

Obviously, the $\eta^4\text{-C}_4\text{Ph}_4$ group of **9** is derived from a coordinated and an added diphenylacetylene. Theoretical analyses of $d^6 \text{M}(\text{alkyne})_3(\text{L})$ complexes suggest that¹³ the three alkyne ligands can donate a total of only 10 electrons to the tungsten atom, while one of the symmetry-adapted alkyne π_\perp orbitals has no match among the metal s, p, or d orbitals. It is probable that this unused alkyne π_\perp orbital of **8** interacts with a π orbital of incoming diphenylacetylene to generate a metallacyclopentadiene intermediate, $(\text{WC}_4\text{Ph}_4)(\text{NCMe})(\text{PhC}\equiv\text{CPh})_2$ (**i**), followed by ring closing to yield **9** (Scheme 3). Alternative pathways *via* concomitant coupling of two coordinated $\text{PhC}\equiv\text{CPh}$ ligands when the incoming diphenylacetylene is added to the metal or by preformation of a tetraalkyne complex, $\text{W}(\text{NCMe})(\text{PhC}\equiv\text{CPh})_4$, would show the ^{13}C label in the alkyne ligands of **9**. Apparently, transformation from **8** to **i** involves an oxidative-addition reaction, where the alkynes are reduced with concomitant carbon–carbon bond formation and the metal loses two electrons. Thus, the

(33) Herrmann, W. A.; Herdtweck, E.; Floel, M.; Kulpe, J.; Küsthardt, U.; Okuda, J. *Polyhedron* **1987**, *6*, 1165.

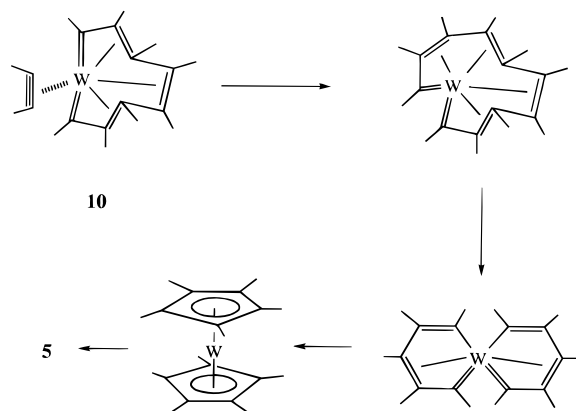
Scheme 3



fact that compound **8** presents higher reactivity toward diphenylacetylene than **1** can be due to the stronger σ -donating and weaker π -accepting ability of the NCMc ligand relative to CO, making the tungsten center of **8** more electron rich to be oxidized.

It is apparent **i** is a reactive molecule, which immediately undergoes reductive cyclization to give **9** or, in the presence of free diphenylacetylene, undergoes alkyne substitution and insertion reactions to lead to **10**. Two pathways shown in Scheme 3 can then be drawn, which differ only with respect to the crucial insertion reactions. The right path from **iv** to **10**

Scheme 4



involves insertion of two alkyne ligands into the metal–carbocycle bonds, thus bringing the cyclobutadiene carbons regiospecifically into the γ - and δ -positions of the metallacycle. On the other hand, the left path from **ii** to **10** involves alkyne insertion into the metallacycle randomly and would scramble the ^{13}C label, consistent with the observations.

Formation of metallacyclopentadiene from oxidative cyclization of two alkynes with metal has been well established.³⁴ For instance, Singleton³⁵ reported cyclo-dimerization of phenylacetylene at a ruthenium(II) center to generate $\text{CpBr}(\text{RuC}_4\text{H}_2\text{Ph}_2)$. Transformation of metallacyclopentadienes into cyclobutadienes is also known, as exemplified by the thermolysis of $\text{Cp}(\text{CoC}_4\text{Ph}_4)(\text{PPh}_3)$, which gives $\text{CpCo}(\eta^4\text{-C}_4\text{Ph}_4)$.³⁶ The conversion **9** \rightarrow **10** represents an interesting ring expansion reaction. Green³⁷ has previously reported the reaction of $[\text{CpRu}(\text{NCMe})(\eta^4\text{-C}_4\text{Ph}_4)]^+$ and $\text{PhC}\equiv\text{CPh}$ to afford the arene complex $[\text{CpRu}(\eta^6\text{-C}_6\text{Ph}_6)]^+$, presumably through an intermediate analogous to **v**.

Possible Mechanism for Transformation of 10 into 3, 4, and 5. We do not have mechanistic information. It is likely that thermolysis of compound **10** induces further alkyne insertion to generate the metallacycloundecaheptaene species $\text{WC}_{10}\text{Ph}_{10}$, followed by C–C bond activation to produce *spiro*- $\text{W}(\text{C}_5\text{Ph}_5)_2$ (Scheme 4). Subsequent steps apparently involve 1,1'-cyclization to yield tungstenocene, $\text{W}(\eta^5\text{-C}_5\text{Ph}_5)_2$, and oligomerization to afford **5**. However, the reaction pathways involving two or more tungsten centers or involving alkylidyne intermediates cannot be ruled out. Schrock has shown³⁸ the formation of substituted cyclopentadienide complexes of W by coupling of alkynes with alkylidyne ligands.

In the presence of CO, the metallacycle of **10** might switch its bonding mode, thus providing a coordination site for a carbonyl ligand. Succeeding reactions are likely 1,5-cyclization to generate **3** or rearrangement of

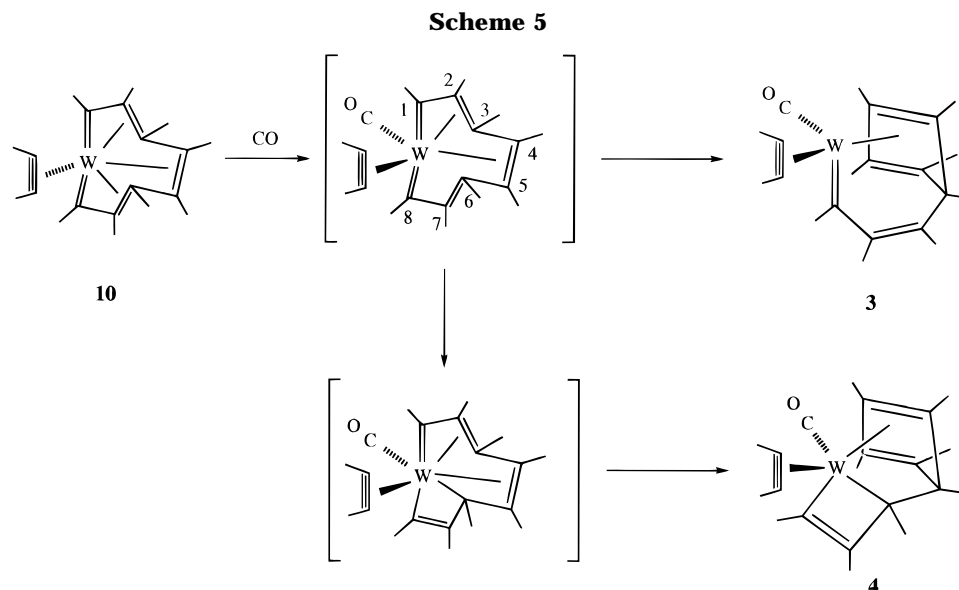
(34) (a) Agh-Ataby, N. M.; Davidson, J. L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1399. (b) Davidson, J. L. *J. Chem. Soc., Chem. Commun.* **1983**, 1667. (c) Davidson, J. L. *J. Chem. Soc., Dalton Trans.* **1987**, 2715. (d) Hirpo, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1988**, *110*, 5218. (e) Porschke, K.-R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1288.

(35) Albers, M. O.; de Waal, D. J. A.; Liles, D. C.; Robinson, D. J.; Singleton, E.; Wiege, M. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1680.

(36) Yamazaki, H.; Nagihara, N. *J. Organomet. Chem.* **1970**, *21*, 431.

(37) Crocker, M.; Green, M.; Orpen, A. G.; Thomas, D. M. *J. Chem. Soc., Chem. Commun.* **1984**, 1141.

(38) Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574.



the propenylidene moiety into a metallacyclobutene ring followed by 1,5-cyclization to yield **4** (Scheme 5).

Conclusions

The results presented here describe interesting products from oligomerization of diphenylacetylene at a tungsten center, where cyclobutadiene complexes (**2**, **9**), cyclopentadiene complexes (**3**, **4**), cyclopentadienyl complexes (**5**, **6**, and **7**), and a metallacyclononapentaene complex (**10**) are obtained.

It is clear that the cyclobutadiene group of **9** is derived from a coordinated and an added diphenylacetylene. A metallacyclopentadiene intermediate is likely involved, followed by ring closing to give **9** or alkyne insertion to

afford **10**. Insertion of alkyne ligands into the metal-carbocycle bonds of **9** also leads to **10**.

An unusual $\eta^3:\eta^2$ -bonding mode has been observed for the C_5Ph_5 groups of **7**. This "localized" feature is likely due to steric repulsions between bulky phenyl groups.

Acknowledgment. We are grateful for support of this work by the National Science Council of Taiwan.

Supporting Information Available: Complete tables of crystallographic data, positional parameters, anisotropic thermal parameters, bond lengths and angles, and torsional angles of **7** and **10** (76 pages). Ordering information is given on any current masthead page.

OM9702340